enhanced helium lines; but as the theory has not yet been extended successfully to the arc lines of the heavier elements, the comparison is of no great value.

I should like to express my indebtedness to Mr. S. Barratt for his help in making the measurements, and to Mr. Fensom for his skilful assistance.

The Adsorption of Gas by Charcoal, Silica, and other Substances.

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1. *Introduction.*

The experimental work here described was carried out on behalf of the Oxygen Research Committee and the Mine Rescue Apparatus Research Committee of the Scientific and Industrial Research Department. The main object of the experiments was to investigate the possibility of obtaining a non-inflammable substitute for the activated charcoal used in metal vacuum flasks intended for holding liquid air. The work was eventually extended so as to include an examination into some of the more theoretical aspects of gas adsorption.

The special problems presented by the metal vacuum vessel made it necessary to pay particular attention to the adsorption of nitrogen at liquid air temperature. Many measurements have also been made using hydrogen.

2. *Preparation of Non-inflammable Adsorbents; their Capacity at Liquid Air Temperature.*

A large number of non-inflammable substances were prepared and were tested to ascertain their capacity for nitrogen at the temperature of boiling liquid air and at normal pressure. The liquid air used had an average composition of 50 per cent. oxygen and 50 per cent. nitrogen; this mixture boils at −190° C. The materials, which were in the granular state, were tested in a uniform manner. Immediately before being used, each sample was heated in a gas-oven for several hours at a temperature of 300° C. The sample was inserted, while hot, into a hot brass retort, holding 25 c.c., and well shaken down. A cap, having a copper tube brazed into it, was screwed to the retort and a pressure test was applied to try the joint; the tube was then connected to a large gas-burette, containing nitrogen standing over strong sulphuric acid. The retort being placed in a bath of cold water, which furnished a definite initial temperature, the burette was read. The retort was then immersed in liquid air and allowed to stay there until no more gas was drawn in. After the state of saturation had been reached, the retort was withdrawn from the liquid air and allowed to regain its original temperature; the volume of gas expelled was measured as a check on the volume absorbed during cooling. A blank experiment made with an empty thimble gave the correction to be applied for contraction of the gas in the thimble and connecting pipe and for condensation upon the metal surfaces.

Of the mineral substances tried meerschaum proved the best, though its capacity at −190° C. was greatly inferior to that of the better kinds of charcoal and silica. Preparations of colloidal alumina and stannic acid were also tried, but were found of little value.

In the following Table, the gas volumes are expressed at N.T.P., and they relate to the amount adsorbed between 18° C. and −190° C. "Gross volume" includes the interstitial spaces, or voids, between the granules.

Table I.—Adsorption of Nitrogen and Hydrogen at Liquid Air Temperature and Atmospheric Pressure.

No.	Substance.	Dry nitrogen.		Dry hydrogen.		$\frac{\text{Hydrogen}}{\text{Nitrogen}}$.
		C.cs. adsorbed per c.c. (gross vol.) of substance.	C.cs. adsorbed per grm. of substance.	C.cs. adsorbed per c.c. (gross vol.) of substance.	C.cs. adsorbed per grm. of substance.	
1	Cocoanut charcoal (activated by steaming)	129	247	66·3	127	0·60
2	Plumstone charcoal (activated)	91·2	—	56·7	—	0·72
3	Birch charcoal (activated)......	44·5	202	27·0	123	0·62
4	German impregnated charcoal (1918)	121	303	25·5	63·8	0·28
5	Blood charcoal	91·1	—	36·3	—	0·40
6	Sutcliffe-Speakman's preparation of briquetted coal and charcoal dusts	91·8	206	43·1	96·7	0·47
7	Cleveland (U.S.A.) activated anthracite	84·9	89·7	53·1	56·3	0·63
8	Graphite, ground	5·6	—	2·7	—	0·49
9	Colloidal silica....................	203	376	26·7	51·6	0·13
10	Dried silica gel (Baltimore, U.S.A.)	115	142	—	—	—

A silica (No. 9) can now be made whose capacity for nitrogen, at −190° C. and atmospheric pressure, is, on the volumetric basis, greater than that of the best charcoal by 66 per cent. The secret of preparation of a high-capacity silica mainly lies in the temperature of drying and in the thorough cleansing of the substance of common salt. The optimum temperature was found to be 300° C. Many ways of de-watering and washing the gel were tried, the most satisfactory being the following:—The unwashed gel (made from water glass) was dried at 300° C. in a gas-oven and plunged while hot into hot distilled water. Washing by decantation was continued until the wash-water was free of chloride; the substance was then dried in the oven for a second time, and was again plunged into hot water, the cycle of operations being continued until the material, when dropped into water, yielded no trace of chloride. As a final test, some of the silica was boiled with weak silver nitrate solution, to make sure that there was no opalescence. This treatment gave better results than dialysis. Drying in the gas-furnace at a steady temperature of 300° C. proved preferable to drying by electric endosmosis. A large number of preparations were made in which the silica was mixed at the sol stage with organic sols such as agar and Irish moss, in order to produce a carbonaceous silica, but the adsorptive capacity was not improved thereby. It was found that carbon in small amount could be introduced by heating the silica and placing it in thick smoke, but again the treatment gave no advantage. The addition of an iron salt to the silica sol proved to be deleterious. Heating the pure silica to 900° C. for a short time, to dispel the last portion of its combined moisture, also resulted in a decrease of capacity.

3. *Preferential Adsorption.*

The phenomenon of preferential gas adsorption is revealed most clearly when the properties of two or more adsorbents are compared. Thus the striking partiality of charcoal and carbonaceous adsorbents for hydrogen stands out in high relief when those substances are contrasted with silica, as is to be seen by the last column of Table I, in which is given the ratio between the hydrogen and nitrogen adsorbed.

In discussing a recent paper by N. K. Chaney (1), H. H. Sheldon stated that he had succeeded in making a charcoal which, at liquid air temperature, was more active upon hydrogen than upon nitrogen; the three examples he quoted give H/N ratios af 1·3, 1·2 and 2·1 respectively.

It seems necessary to assume the existence of a high specific attraction between the molecules of the two elements, carbon and hydrogen. That the preference does not result from the state of porosity of the adsorbent is indicated by the fact that the non-porous graphite (No. 8) was found to have at −190° C., a H/N ratio much the same as that of the very porous blood charcoal (No. 5).

4. *Determination of Density and of the Solid and Gaseous Volumes of Charcoal and Silica.*

In a sample of granulated charcoal or silica the gross volume is made up of:—

(*a*) The volume of the solid.

(*b*) The interstitial volume, *i.e.*, that of the open spaces, or voids, between the granules.

(*c*) The volume of the capillaries and polymeral interstices existing within the granule; this being spoken of below as the *internal gaseous volume.*

It was important to ascertain the relation between these volumes, and especially between (*a*) and (*c*).

Mitscherlich (3), employing the immersion method, found the charcoals used by him to consist, in the piece, of about 39 per cent. of solid matter and 61 per cent. of internal gaseous volume. W. D. Harkins and D. T. Ewing (3) ascertained the "pore" volume to range between 53·4 per cent. when water, and 59·3 per cent. when pentane was the liquid used. E. B. Miller (4) and his associates estimated that in dried silica gel (No. 10, Table I) the internal gaseous volume was 41 per cent. of that of a granule.

In obtaining the solid volume, I placed the sample, whether of charcoal or of silica, in a dry graduated tube; shook it well down, and observed its gross volume. Its weight *in vacuo* was next found. The sample was then heated and thoroughly evacuated by being connected, through a three-way tap, to a much larger bulb holding dry cocoanut charcoal and immersed in liquid air. After cooling the sample, the tap was turned and air-free water was allowed to enter the exhausted tube to a definite mark. The routine then followed that of the ordinary specific gravity bottle method. As has been shown by Harking and Ewing (3) and by A. M. Williams (5), the specific gravity and, therefore, the proportional volume of the solid determined in this way is affected by error, due to the high density of the layer of liquid actually in contact with the solid. It is clear that, under the agency of the error in question, a specific gravity so computed will be too high; that the more active the adsorbent the more serious will be the error involved, and also that the error will increase with the compressibility of the liquid employed. Williams has discussed (5) the possible incidence of another factor militating against the accuracy of the results obtained by the immersion method, namely that of inadequate penetration, especially by large molecules such as those of chloroform, into the more minute intermolecular openings of the solid. An error of this character, however, would operate in the opposite sense to that due to compressibility and would tend to reduce the latter; further, when water is the liquid used it is difficult to imagine that there can be, in any part of a charcoal, an opening so small that the water molecule cannot enter, looking to the fact that these channels have been the vents through which larger hydrocarbon molecules made their escape during the carbonising process. In silica, again, where water was the only compound driven off in the gaseous condition during treatment, the passages through the solid must have served in the first place for the egress of steam, and, therefore, they are presumably accessible to the water molecule, though not necessarily to larger molecules.

Harkins and Ewing (3) found that the density of a certain activated cocoanut charcoal, as ascertained by immersion, varied between 1·843 when water was used, to 2·129 when pentane was employed. Other densities of cocoanut charcoal (ascertained by water-immersion) quoted by these workers are: 1·863, 1·835, 1·808; Titoff (6) gave 1·86, Baerwald (7) 1·92 and Miss Homfray 1·66. Hulett (quoted by Chaney (1)) got the value 1·84. I found the density of activated cocoanut charcoal (No. 1, Table I) to be 1·88, and that of "raw" cocoanut charcoal to be 1·74. For the reasons given, the former value is certainly higher than the true density.

Williams (5) found the specific volume of blood charcoal, by immersion in chloroform at 25° C., to be 0·46; by an able theoretical analysis based upon the experimental facts he then shows that, owing to compression of the chloroform, this value was too low by 0·21. That is to say, the true specific volume of the blood charcoal he used was 0·67 c.c. per gramme, and the equivalent density was 1·49. He had previously determined the density by water-immersion to be 1·96—a figure which therefore turned out to be 32 per cent. higher than the true value.

The intensity of the forces of attraction at the surfaces of such a silica as No. 9, Table I, though greatly less than in the case of charcoal, is appreciable, and, in consequence, the specific gravity of the silica ascertained by the immersion method is also apt to be too high. As will subsequently appear, it is possible with silica to de-activate it completely; hence the apparent density in the inactive and active states may easily be compared. The water-immersion method gave 2·30 as the specific gravity of No. 9 and 2·00 as that ratio after de-activation. The difference would doubtless have been greater but for the fact that, during de-activation, the silica lost combined water.

In the case of cocoanut charcoal the most satisfactory way of measuring the proportion of *interstitial space* between the granules was to place a sample, well shaken down, in a wide tube of known volume, the inlet and outlet to the tube being by capillary stems into which the granules were too large to enter, and then to fill the interstices by admitting mercury. As the mercury did not wet the charcoal, the adsorbed gas remained quiescent. The volume of mercury entering between the granules was found by weighing.

With only one of these substances was it found possible to get a reliable direct measurement of internal gaseous volume, namely with the de-activated variety of silica to which allusion has already been made. This was done by means of a glass apparatus which enabled a sample of silica to be evacuated under water; after exhaustion normal pressure was restored, the gas emitted by the silica was discharged from the apparatus, and the volume of water entering the "pores" was measured on a capillary stem. The measurement was reasonably reliable because de-activated silica has zero retentivity; therefore it parted with its gas readily under the influence of the relatively imperfect vacuum applied, and the water did not pass under compression when it entered the internal spaces vacated by the air.

De-activated silica was found in this way to have an internal gaseous volume amounting to 6 per cent. of the gross volume.

The figures of the following Table do not take into account the compressibility of water and must merely be regarded as providing a first estimate, which will need revision at a later stage. Obviously, with the two active substances, the whole of the error affecting the evaluation of the solid volume affects that of the internal gaseous volume, and as the former is too low the latter must be too high.

Table II.—Estimates of the Proportional Volume of Solid Matter, Internal Spaces and of Voids, uncorrected for Effect of Compressibility of Water.

Substance.	Volume of solid matter.	Internal gaseous volume.	Interstitial space.
	per cent.	per cent.	per cent.
Activated cocoanut charcoal (No. 1, Table I)	28	32	40
Activated colloidal silica (No. 9, Table I) ...	27	30	43
De-activated silica	51	6	43

According to these values, the internal gaseous volume constitutes 53 per cent. of the volume of a granule of the charcoal; the equivalent proportions for granules of active and de-activated silica are 53 and 10½ per cent. respectively.

5. *State of Adsorbed Gas; Further Consideration of the Density of the Solid Matter.*

The volume of dry nitrogen taken in at atmospheric pressure and 18° C. was determined for dry cocoanut charcoal (No. 1, Table I) and dry silica (No. 9). The sample was placed while hot in the brass retort, well shaken down; the cap (with copper tube attached) screwed tightly into place, and the joint tested for leakage. The tube was connected to a burette containing nitrogen, standing over strong sulphuric acid. The retort having been placed in a water bath at 18° C., the burette was read. The retort was then put in a small electric pot furnace, the temperature was slowly raised above 300° C., and the volume expelled measured. The retort was then cooled and the volume drawn in again observed. By alternately heating and cooling several times in this manner a reliable mean value was obtained. The mean was corrected by subtracting the volumetric difference due to simple expansion or contraction between the temperature extremes, which was ascertained from a blank experiment. The results are given on the first line of Table III; the second line is copied from Table I.

Table III.—Adsorption of Dry Nitrogen at Atmospheric Pressure, per c.c. of Gross Volume.

	Cocoanut charcoal.	Silica.
	c.cs. (N.T.P.).	c.cs. (N.T.P.).
Adsorbed at 18° C.	5·5	5·5
Adsorbed between 18° C. and −190° C.	129	203
Total adsorbed at −190° C.	134·5	204·6

Dewar (9), making use of Mitscherlich's value for the internal gaseous space (*vide sup.*), estimated the density of nitrogen adsorbed in charcoal at the boiling-point of the gas to be 1·00, a value approximating to the density of solid nitrogen, 1·026. We may now attempt a similar estimation by the aid of the figures of Tables II and III. Thus, in the case of silica, 204·6 c.cs. of nitrogen at N.T.P. (Table IV) weigh 0·256 grm., and if, as Table II may lead one to infer, this mass is condensed in a volume of 0·30 c.c., its *average* density, when adsorbed at −190° C., must be 0·83. A similar determination for the charcoal gives 0·53 as the density of the adsorbed nitrogen at the same temperature. The density of liquid nitrogen, according to Baly and Donnan (10), is 0·808 at −195° C. (its boiling-point at N.P.) and 0·785 at −190° C.

Judging from the stated result for silica, the density of the adsorbed gas exceeds that of the liquid at the temperature in question, but it would appear that the reverse is true for charcoal. We know, however, that the specific attraction—*i.e.*, the force subsisting between the solid and the gas molecules—is much greater with charcoal than with silica, and on that account would expect the nitrogen to be held in a denser condition in the charcoal. We also know from Dewar's experiments on the heat of adsorption (11), and from the observations and calculations of Williams (5) and others, that, in the stated circumstances, the gas must exist in charcoal in a state which is denser than the liquid. Clearly, then, the above estimate (0·53) of the specific gravity of the nitrogen adsorbed in charcoal is too low. The error is due to the fact that when Table II was drawn up, no account was taken of the compressibility of the water used in determining the density of the charcoal. In consequence (see Section 4), the estimate of internal gaseous volume was too high; hence the computed specific gravity of the adsorbed gas is too low. For the same reason, the value (0·83) for the density of the nitrogen adsorbed by silica will also be too low, though the error will, in this case, not be so large.

If 0·83 be assumed to be the correct value in the instance of cocoanut charcoal (and the evidence, as we have just seen, points to this being a low estimate), the internal gaseous volume amounts to only 20·4 per cent. of the gross volume of the granules; the volume of the solid matter amounts to 39·6 per cent. and the true density of the charcoal works out at 1·33. It may therefore be safely inferred that the true density of the cocoanut charcoal I used was under 1·33, instead of being 1·88, as appeared from the water-immersion determination.

So far attention has been principally focussed upon the case in which an adsorbent has been allowed to saturate itself at normal pressure and at a temperature only a few degrees above the boiling-point of the gas adsorbed. Let us now consider the other extreme, namely, the adsorption of a gas at low pressure or low partial pressure. In these circumstances the action differs markedly from that at high concentrations in that it follows Henry's law (2, 12). The same holds true, very nearly, for the adsorption of gases like nitrogen, oxygen, or hydrogen at ordinary temperature and moderate pressures, and, as Miller's recent work shows (4), for SO_2 adsorbed by silica at temperatures of 100° C. or more. At these low concentrations the attraction of the gas molecules for each other must be an influence altogether negligible in comparison with the attraction between the gas and the solid—a force which Williams (5) calculates to be such that it is able to cause an aggregation of adsorbed molecules upon the surface of activated charcoal equivalent to that resulting from a pressure of about 10,000 atmospheres.

Adsorption at low concentrations must depend, then, upon (*a*) the magnitude of this attraction (the specific attraction of the solid), and (*b*) the extent of solid surface exposed to the gas. It will not depend upon the internal gaseous volume, since that volume is no criterion of the exposed surface.

As the concentration is increased, the packing of the gas molecules upon the surfaces will also increase in density. Sooner or later a stage will be reached at which the gas molecules can only accumulate by adhering to others already anchored, and then the attraction of the molecules for each other will become a factor of importance. Eventually, as the temperature and pressure become such as to bring the outside gas near to liquefaction, the adsorption of gas molecules upon surfaces consisting of anchored gas molecules will proceed at an intensified rate; the finer, and finally the coarser, capillaries will fill up. The volume of gas (expressed at N.T.P.) which can be taken in at complete saturation will depend upon (*a*) the specific attraction of the solid as determining the firmness of anchorage of the initial layer and the degree of compression of that layer; (*b*) the thickness of the layer of compression; (*c*) the exposed surface as determining the extent of the layer of compression; (*d*) the compressibility of the liquefied gas; (*e*) the "internal gaseous volume" of the adsorbent, now filled with liquid; and (*f*) the relation between the densities of the gas and its liquid.

As the attachment of gas molecule to gas molecule at this latter stage cannot of itself produce a mass denser than the liquid at the particular temperature, and, as the average density of the adsorbed gas has, in these circumstances, been shown to be greater than that of the liquid, it follows that the attraction of the solid for the gas molecule is greater than the attraction of the gas molecules for each other. It seems likely that we have, in this latter relation, one of the conditions essential to adsorption.

The differences between the characteristics of adsorption at low and high concentrations make it impossible to judge of the former from the volume of gas taken in during complete saturation; hence the figures of Table I bear no relation to the retentivity of the substances. Because it has a high capacity for nitrogen at normal pressure and -190° C., a substance is not necessarily suitable for producing high vacua.

When the state of complete saturation is at hand, each granule will be surrounded by a thin halo or envelope of condensed gas. The condensation effected by graphite, which has zero internal gaseous volume, must be entirely due to such an envelope, and, as Table I shows, this is by no means negligible with nitrogen 5° above the boiling point of the gas. The argument used earlier in this Section, to the effect that at complete saturation the internal gaseous volume is altogether occupied by liquid, should, strictly speaking, be modified to the extent needed to take this envelope into account. The correction implied would slightly reduce the computed average density of the adsorbed gas, though not sufficiently to affect the conclusions drawn.

6. *The Constitution of an Adsorbent.*

When we turn from a consideration of the gas adsorbed to an analysis of the characteristics of the solid substance, which acts both as condenser and as reservoir for that gas, we meet with phenomena, such as that of activation, whose effects can be studied by experiment, but whose intrinsic nature, to a great degree, yet remains in doubt.

It is unsatisfactory to speak of gas molecules being condensed upon the surface of the solid, since, if the gas is to be referred to the molar scale, so must the solid; such a statement, indeed, compels the question, The surface of what? In the present state of our knowledge of the constitution of solids, there appears to be no clear answer to that question; we are reasonably sure, however, that, in solid substances such as carbon and silica, we are not dealing with the ultimate molecule* but with elaborate polymers.

Apparently, the only solid structures which are impervious to gas are the crystal and the glass. As is well known, the former can hold indefinitely gas "included" under pressure, while the latter, whether common glass, vitreous porcelain, or fused silica, can hold a high vacuum—and there is no better test of tightness—as long as the character of the glass remains unchanged. That these two forms possess so unusual a characteristic in common makes it probable that they have analogous structures; that, in fact, in place of being a molecular aggregate (which would be pervious to gas), a piece of glass, like a crystal, is a single atomic linkage, and as such is entirely free from interstices on the molar scale. If this view be allowed, it is clear that an adsorbent must be non-vitreous—an aspect of the question which is further considered below.

It has already been seen, in Section 3, that the chemical character of the material affects its properties as a gas-adsorbent. With any given material, there are two factors which have a profound influence on adsorptive power, namely, (*a*) the degree of canalisation of the substance, *i.e.*, its porosity on the microscopic or ultramicroscopic scale, and (*b*) the degree of porosity on the molar scale.

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* I am indebted to Sir James Walker for suggesting the expression "ultimate molecule" to distinguish between H_2O and $H_{2n}O_n$, for example, or between the ultimate molecule SiO_2 and the polymeride $n(SiO_2)$. The expression removes much of the ambiguity of meaning attaching to the word "molecule," which is not now always used in the original sense.

The microscopic or ultramicroscopic canals, whose presence as an intricate network of connected passages is so striking a feature of a high-capacity adsorbent, important though their function is, do not alone determine adsorptive power. A high-capacity silica may be de-activated by prolonged heating, and though, in the de-activated state, one-fifth of the original internal gaseous volume remains, the amount of gas it can take in is virtually *nil* even at liquid air temperature. Evidently the capillaries are only of use when they traverse a medium in a suitable physical condition. Again, powdered graphite, which has no capillary passages, is able to adsorb 5·6 times its gross volume of nitrogen at −190° C.

The largest canals of charcoal can be seen under the microscope and Saussure, who measured the size of the cells of charred wood, found them to be, on the average, 10^{-3} cm. in diameter, or about 13,000 times the diameter of a nitrogen or oxygen molecule. On the other hand, Lamb, Wilson and Chaney (13), from a study of the vapour-pressure curves of adsorbed liquids, estimated the average diameter of the pores (assumed to be cylindrical) of activated charcoal—including the finest with the coarsest openings—to be about 5×10^{-7} cm., which is less than seven times the diameter of the gas molecule. It may be inferred from these figures that the greater part of the internal gaseous space of an efficient adsorbent consists of passages which are not greatly larger than the gas molecule.

To draw an analogy: the coarser canals traversing the adsorbent may be compared with the bronchi of the lungs and the finer openings with the alveoli. Either kind of passage is useless without the other and their functions differ: the coarser canals convey and distribute the gas with a minimum of impediment, but (excepting in conditions approaching total saturation) they do not hold it; the gas is chiefly held on the surfaces of the polymers in openings of molar dimensions.

It will be evident that a higher degree of porosity on the molar scale and a greater exposure of surface will occur when the polymers are small rather than large; and that (other conditions remaining constant) if we can disrupt the elaborate polymers which build up a solid, the more active the material will become in adsorbing gas.

Reference has already been made to the fact that a high-capacity silica may be converted into a non-adsorptive substance by heating. The change is not due to the destruction of the capillaries, for 20 per cent. of the original porosity remains after heating. Had adsorption been merely a matter of pore-space, one-fifth of the original capacity—or, at −190° C., about forty volumes of nitrogen per volume of silica—would have survived. Actually, the capacity fell almost to zero. The question arises: What happened to this silica to cause de-activation? The microscope showed the particles to be unchanged in outward form, but here and there in the mass there was evidence of incipient fusion, which was revealed by the occasional presence of a few of the finest particles enclosed by a skin. At first it was thought that the formation of surface skins might explain the loss of adsorptive power, but when a sample was finely ground there was no improvement: the change had affected the whole mass.

The evidence favours the explanation that the heating, without destroying the coarser passages, had vitrefied the silica, and blotted out the finest openings upon which adsorption so largely depends. In other words, the heating had converted a granule which was originally an aggregate of small polymers riddled with openings into a completely polymerised unit impermeable on the molar scale.

7. *Activation.*

It has long been known that if charcoal, and preferably a dense charcoal, be subjected to long-continued heating in the presence of a small amount of oxygen, its power of adsorption is greatly increased. This, the earliest process of activation, was developed by Dewar in connection with the charcoal used by him for obtaining high vacua; it has been discussed lately by Philip, Dunnill and Workman (14). Recently, it was discovered in this country that activation could be secured in a shorter time by the use of superheated steam, and this process, known as the steaming process, was considerably used towards the end of the war, both in America and Great Britain. Lamb, Wilson, and Chaney (13) state 350° to 450° to be the optimum temperature in the older, or air-activation process, though in this country it has been usual to carry it out at a considerably higher temperature. These writers advance the theory that activation mainly results from driving off the hydrocarbons which are residual in raw charcoal. No doubt the clearing of the charcoal of these substances is beneficial; but that it forms the chief object in activation is unlikely. The theory falls under three objections: First, the small amount of volatile hydrocarbon which is left to be driven off in this manner is disproportionate to the result produced. Secondly, though the presence of oxygen would help in breaking up the hydrocarbons, it would not be essential to their ejection; actually oxygen is found to be a necessity in the activation of charcoal (14). And thirdly, the residual hydrocarbons, as Chaney (1) has shown, require a temperature exceeding 1000° C. before they are all dispelled—a fact which appears difficult to square with the theory if 350° to 450° is the optimum in air-activation. Chaney's later hypothesis (1), that active and inactive charcoal are different isotropes, does not seem to be sufficiently supported by evidence.

The most probable explanation of the activation of charcoal would appear to be that, in common with other highly polymerised substances, its structure is apt to be simplified by heat. Heating to 1000° C. without oxygen has no permanent effect. In other words, any cleavage or simplification of the polymers which may result from raising the temperature in a reducing atmosphere is followed by a re-union on cooling. But, if a little oxygen (either from air or from steam) be available when the polymers are split, some of the carbon is removed as CO_2; their cleavage is perpetuated; the porosity on the polar scale is increased, and with it the surface accessible to gas.

Obviously, oxygen cannot serve in the case of silica the same useful purpose that it does for charcoal during activation, and to break down the silica polymer dependence has to be placed on water. The preparation of silica from the hydrogel by heating involves the driving off of large proportions of water, different proportions being expelled as the temperature is raised by given increments. As much, if not most, of this water is chemically combined with the silica, exsiccation will tend to break up the polymers. The last modicum of moisture is held with great tenacity, and is only driven away at a temperature exceeding 700° C. No. 9, Table I, for example, was one which had not been raised to this temperature, and it therefore held the residual moisture in combination. As a means of activation, the expulsion of water from silica is much less effectual than the heating and partial oxidation of charcoal; the latter method gains by the fact that it can be continued for several hours or days.

The influence of heat upon colloidal silica, apart from the effect of dehydration just referred to, has certain points of interest. A silica which has been imperfectly cleansed of sodium chloride will, on heating, fuze into a glass of negligible adsorptive capacity. A silica chemically clean of chloride, but which was adulterated in the sol stage with carbonaceous matter, as, for example, with seaweed sol, will, if heated above 750° C., yield considerable volumes of carbon dioxide, carbon monoxide, and hydrogen through the interaction of the residual moisture and the carbonaceous matter. A chemically clean silica of very high capacity at low temperature, if heated by the blowpipe for a few minutes *circa* 900° C. so as to drive off most of the residual water, is not affected in its capacity for nitrogen at liquid air temperature; but, if the same silica be kept in the electric furnace for five or six hours at 1000° C., its adsorptive power is destroyed, and, if heated for a few hours at 750° to 900° C., it loses a considerable part of that power. We have here an example of an activated substance being de-activated by prolonged heating. The bearing of this result upon the problem of gas adsorption has already been discussed.

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Summary.

Section 2.—The method of determining the adsorptive capacity of a substance at liquid air temperature is described, and results are given of the capacity of silica and certain charcoals.

Section 3.—Charcoal and silica are compared, especially as relates to nitrogen and hydrogen, to illustrate preferential adsorption and to exemplify the influence of chemical composition on gas adsorption.

Section 4.—The effect of the compressibility of the initial layer, when the density of an adsorbent is determined by the immersion method, is considered. An evaluation is made of (*a*) the volume of solid matter, (*b*) that of the interstitial space between the granules, and (*c*) that of the internal gaseous space for silica and cocoanut charcoal.

Section 5.—The density of the nitrogen adsorbed at −190° C. by silica and charcoal is calculated from experimental data. From these results it becomes possible roughly to estimate the error affecting the density of charcoal ascertained from water immersion, and it is concluded that that method gave a result for the writer's cocoanut charcoal which was at least 0·55 too high. The conditions affecting adsorption at low and high saturation are set forth.

Section 6.—The presence of capillaries is not sufficient to account for adsorption. A high capacity silica may be de-activated, and in the inactive state it remains porous. Graphite, which has no pores, adsorbs gas at −190° C. The evidence leads to the conclusion that de-activated silica is vitreous. It is argued that a vitreous solid, like a crystal, is a polymer, *i.e.*, a complete atomic linkage. The importance of distinguishing between the coarser capillaries or canals and the finer interpolymeral openings of an adsorbent is emphasised.

Section 7.—Activation is considered to be the effect of disrupting the solid polymers, and the means of accomplishing the partial depolymerisation of charcoal and silica is described.

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On the Transmission Colours of Sulphur Suspensions.

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1. *Introduction.*

In the 'Proceedings of the Royal Society,'* Keen and Porter described some interesting optical effects exhibited by suspensions of finely-divided sulphur, obtained by adding dilute sulphuric acid to a weak solution of sodium thiosulphate. As is well known, the solution (which is at first perfectly transparent) becomes turbid when the particles form in it, and the transmission of light by the suspension gradually diminishes in intensity. The colour of the transmitted light, which is at first white, also changes, becoming yellow, orange, red, and then deep crimson red. Finally, the solution (if in a sufficiently thick layer) becomes almost completely opaque. This had been previously supposed to terminate the sequence of phenomena. Keen and Porter observed, however, that after further lapse of time, light begins again to be transmitted by the suspension, the colour of the light which passes through being at first indigo, then blue, blue-green, greenish-yellow, and finally again white. This remarkable reappearance of the transmitted light was quantitatively studied by them, measurements being

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* Ser. A, vol. 89, p. 370 (1914).